

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 2001-180363 (71)Applicant : MATSUSHITA ELECTRIC IND CO LTD

(22)Date of filing : 14.06.2001 (72)Inventor : NAGURA KENSUKE  
YAMAMOTO TORU

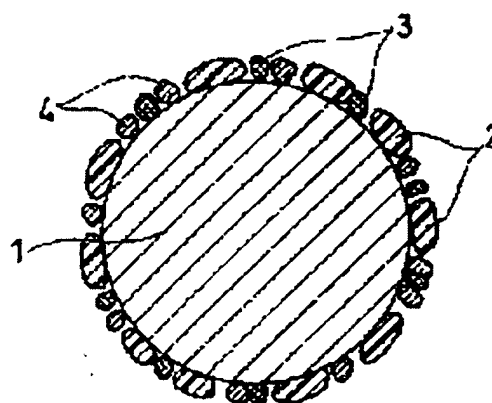
(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the cycle life time of a lithium secondary battery by effectively suppressing problems, such as battery dimensional changes, increase in internal resistance and deterioration of charge and discharge performance with heavy current, resulting from the swelling and contraction of an active material accompanying the charging and discharging of the lithium secondary battery.

SOLUTION: In this lithium secondary battery, the surface of at least one particle of a positive electrode active material and a negative electrode active material is partially covered with a lithium ion conductive polymer.

The active material particle surface of the part which is not covered with the polymer is preferably partially or entirely covered with a conductive agent, or the conductive agent and a lithium ion conductive inorganic solid electrolyte.



- 1 活物質粒子
- 2 リチウムイオン伝導性ポリマー
- 3 導電剤
- 4 リチウムイオン伝導性無機固体電解質

LEGAL STATUS

## TECHNICAL FIELD

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[The technical field to which invention belongs] this invention relates to the lithium secondary battery equipped with the nonaqueous electrolyte of the shape of a liquid, a gel, or a solid-state.

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## PRIOR ART

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[Description of the Prior Art] In recent years, the need of the rechargeable battery as the power supply is very large with the rapid spread of portable devices, such as a personal computer and a cellular phone. Especially a lithium secondary battery is lightweight, it is observed as a rechargeable battery with which the high voltage is obtained, and development and utilization of various cells are advanced actively. The cell using the liquefied organic electrolyte which dissolved lithium salt in the organic solvent among lithium secondary batteries is already completely put in practical use as an object for portable devices, and the cell using the polymer electrolyte of a gel is also put in practical use partly.

Furthermore, there are no worries about a liquid spill and research and development of the lithium secondary battery using the polymer solid electrolyte or the inorganic solid electrolyte of lithium ion conductivity are actively done aiming at the cell in which a miniaturization or thin-shape-izing is possible.

[0003] Generally, a negative-electrode active material expands at the time of charge of a lithium secondary battery, there is an inclination which a positive active material contracts, and there is an inclination which the reverse volume change produces at the time of electric discharge.  $\text{LiCoO}_2$  of a positive active material starts and  $\text{LiMn}_2\text{O}_4$  starts about 3.6% of volume change 3.2% on the usual charge-and-discharge conditions, for example. In alloy system negative electrodes, such as a TiSn alloy, a big cubical expansion happens especially at the time of charge.

[0004] Therefore, in the lithium secondary battery, change of the cell size by charge and discharge, especially expansion of a cell pose a practical big problem. Expansion and contraction of a cell also become the cause of destabilizing contact between electrode-cell containers and increasing the internal resistance of a cell. Furthermore, since the contact degree between components, such as an active material particle in an electrode, an electric conduction agent particle, and an electrolyte, becomes weaker while a positive electrode and a negative electrode repeat expansion and contraction by the charge-and-discharge cycle, there is a problem on which the charge/discharge capability ability in a high current deteriorates especially in a lithium secondary battery.

[0005] An inorganic solid electrolyte is made to contain also in an electrode in all the solid-state lithium secondary batteries that a lithium ion conductivity inorganic solid electrolyte layer is made to intervene between positive/negative poles, and are constituted. Since this inorganic solid electrolyte is hard powder, contact between the particles of an electrolyte and an active material is easy to be

severed by expansion and contraction of the electrode by charge and discharge. Thereby, especially, with all solid-state lithium secondary batteries, supply of the lithium ion to an active material or the path of discharge is intercepted, and there is a problem to which the current in which charge and discharge are possible falls remarkably.

[0006] In order to solve this problem, all the solid-state lithium cells that covered the front face of an active material particle with lithium ion conductivity polymer are proposed (for example, JP, 11-7942, A). This aims at suppressing relaxation of junction between the particles by expansion and contraction of the active material in the inside of the electrode at the time of charge and discharge, and the volume change of a cell with the elasticity of the aforementioned polymer.

[0007] However, since the occupied volume of the polymer layer within an electrode is large when the front face of an active material particle is extensively covered with a polymer layer as indicated in the example, the volume of the opening formed between the active material particles in an electrode decreases remarkably. Therefore, since the polymer of the portion which was compressed at the time of expansion of an active material, and deformed is hardly held in the aforementioned opening but expansion of an active material is reflected in expansion of an electrode as it is, the effect which suppresses expansion of an electrode is scarce. Moreover, since the whole surface of an active material particle is covered with the polymer layer, the network of the electronic conduction between active material particles becomes inadequate, and there is a problem to which a high charge-and-discharge property falls.

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[Translation done.]

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## EFFECT OF THE INVENTION

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[Effect of the Invention] By this invention, the dimensional change of a lithium secondary battery and the increase of internal resistance by charge and discharge can be suppressed effectively. Furthermore, a high-rate-discharge property and a cycle life are sharply improvable.

## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] this invention solves the problem of the above-mentioned conventional lithium secondary battery, and aims at degradation of change of the cell size by charge and discharge, increase of internal resistance, and the charge/discharge capability ability in a high current offering the lithium secondary battery suppressed effectively.

## MEANS

[Means for Solving the Problem] The lithium secondary battery of this invention is characterized by covering partially the front face of one [ at least ] particle of a positive active material and a negative-electrode active material with lithium ion conductivity polymer. As for active material particle front faces other than the portion covered with the aforementioned lithium ion conductivity polymer, it is desirable to be covered with the electric conduction agent partially or extensively. As for active material particle front faces other than the portion covered with the aforementioned lithium ion conductivity polymer, it is still more desirable to be covered with the electric conduction agent and the lithium ion conductivity inorganic solid electrolyte partially or extensively.

[0010]

[Embodiments of the Invention] Drawing 1 is the cross section showing typically the active material particle which carried out covering processing of the front face by this invention. The front face of the active material particle 1 is partially covered with lithium ion conductivity polymer 2. Furthermore, if needed, the active material particle front faces of the portion which is not covered with the aforementioned polymer 2 are the electric conduction agent 3 and the lithium ion conductivity inorganic solid electrolyte 4, and are covered partially or extensively.

[0011] The lithium secondary battery of this invention makes it an indispensable condition to cover partially the front face of the particle of one [ at least ] active material of a positive active material and a negative-electrode active material with lithium ion conductivity polymer. Thereby, degradation of change of the cell size by charge and discharge, increase of internal resistance, and the charge/discharge capability ability in a high current can offer the lithium secondary battery suppressed effectively.

[0012] In this invention, since the layer of lithium ion conductivity polymer is wearing the active material particle front face partially unlike the aforementioned conventional technology (JP, 11-7942, A) and the occupied volume of the polymer layer within an electrode is small, volume of the opening formed between active material particles can be enlarged. When the polymer layer which has flexibility is compressed by this and it deforms by it at the time of expansion of an active material particle, the polymer for the variant part can be held in the aforementioned opening. Thus, expansion of an electrode is eased by absorbing expansion of an active material and deformation of the polymer layer by it within an electrode.

[0013] Furthermore, at the time of contraction of an active material particle, when the polymer previously transformed by expansion of an active material particle reverts to the original form, change of an electrode size is eased. Thus, the volume change of the cell accompanying charge and discharge is eased, and when containing a cell to the predetermined space especially in a device, expansion of the cell which poses a problem can be suppressed effectively. The good contact between an electrode and a cell container is maintained

simultaneously, and increase of the cell internal resistance by the charge-and-discharge cycle can be prevented.

[0014] In this invention, since the portions which are not covered with the polymer layer of the front face of an active material particle can be contacted within an electrode, the network of the electronic conduction between active material particles can fully be formed. Furthermore, since the active material particle is covered by the polymer of lithium ion conductivity, supply of the lithium ion to an active material particle or the path of discharge is fully secured. By these, the high charge-and-discharge property of a cell can be raised.

Furthermore, the junction nature between each particle in an electrode is strengthened by the binding capacity of the lithium ion conductivity polymer covered by the active material particle front face, and even when expansion and contraction of an active material arise at the time of charge and discharge, junction between the aforementioned particles is maintained. Thereby, the charge-and-discharge cycle life of a cell can be raised further.

[0015] As for the lithium secondary battery of this invention, it is desirable that active material particle front faces other than the portion covered with lithium ion conductivity polymer are covered with the electric conduction agent partially or extensively. By covering an active material particle front face with an electric conduction agent, the electronic-conduction nature between active material particles can be raised. Thereby, the internal resistance of a cell can be reduced further and the charge/discharge capability ability in a high current can be raised further.

[0016] As for the lithium secondary battery of this invention, it is still more desirable that active material particle front faces other than the portion covered with lithium ion conductivity polymer are covered with the electric conduction agent and the lithium ion conductivity inorganic solid electrolyte partially or extensively. The usual lithium ion inorganic solid electrolyte is equipped with the ionic conductivity of  $10^{-4}$  -  $10^{-5}$  ohm $^{-1}$  and cm higher 1-2 figures than solid-state-like lithium ion conductivity polymer. Thus, when ionic conductivity makes an inorganic high solid electrolyte adhere to an active material particle front face, the ion conductivity of the active material particle front face partially covered with lithium ion conductivity polymer can be raised further. The effect of the electric conduction agent which raises the electronic-conduction nature between active material particles can join this, and the charge/discharge capability ability in a high current can be raised further.

[0017] Generally, the ionic conductivity of lithium ion conductivity polymer of a solid-state-like thing is as low as  $10^{-5}$  -  $10^{-6}$  ohm $^{-1}$  and cm, and the thing of a gel shows  $10^{-3}$  -  $10^{-4}$  ohm $^{-1}$  and cm, and a high value. Therefore, when ionic conductivity uses low solid-state-like polymer comparatively as lithium ion conductivity polymer, it is effective to use an inorganic solid electrolyte together as mentioned above in order to raise the ionic conductivity on the front face of an active material. When this method is applied to all solid-state lithium secondary batteries, a big effect is acquired especially.

[0018] The polymer of the shape of a solid-state which included lithium salt, such as LiBF<sub>4</sub>, LiPF<sub>6</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, and LiClO<sub>4</sub>, in at least one resin chosen from

the group which consists of acrylonitrile system resins, such as polyester system resins, such as polyether system resins, such as a polyethylene oxide, and polyester terephthalate, an acrylic resin, acrylonitrile, and a vinyl acetate copolymer, and a polyvinylidene-fluoride resin as lithium ion conductivity polymer of this invention can be used.

[0019] There is the following method among the methods of covering an active material particle front face with the lithium ion conductivity polymer of the shape of an aforementioned solid-state partially. First, lithium salt is dissolved in the aforementioned resin which heats and carried out melting, and the powder of polymer is produced by the method of drying, while injecting after cooling the method of pulverizing, or the solution in which an aforementioned resin and aforementioned lithium salt were dissolved in hot blast etc. Subsequently, an active material particle front face is covered if needed using this polymer powder with the powder of an electric conduction agent and a lithium ion conductivity inorganic solid electrolyte. Under the present circumstances, polymer powder is wearing an active material particle front face partially, and the powder of an electric conduction agent and an inorganic solid electrolyte covers so that active material particle front faces other than the portion covered with polymer powder may be worn partially or extensively.

[0020] The method of putting in active material powder in equipment from active material powder with coating with a smaller particle size, i.e., polymer powder, polymer powder and the mixed powder of an electric conduction agent, or the powder that mixed inorganic solid electrolyte powder further, and performing covering processing mechanically as [ both ] the covering method, is desirable. As the method of mechanical covering processing, methods, such as the mechanical milling method by the hybridization method, the mechanofusion method, a planet ball mill, a ball mill, etc., can be taken. Otherwise, methods, such as chemical coating processing which deposits polymer powder and a metal electric conduction agent on an active material particle front face, can also be taken by non-electrolyzed compound plating in the dispersion liquid of polymer powder and a metal electric conduction agent.

[0021] The polymer of the gel which contains organic solvents, such as ethylene carbonate, polypropylene carbonate, ethyl methyl carbonate, dimethyl carbonate, and gamma-butyrolactone, or these mixed solvents in the lithium ion conductivity polymer of the shape of an above solid-state further as lithium ion conductivity polymer of this invention can also be used. Since ionic conductivity is high, the gelled lithium ion conductivity polymer is much more effective in order to raise the high charge-and-discharge property of a cell.

[0022] The following method can be taken as a method of covering the lithium ion conductivity polymer of a gel partially on an active material particle front face. First, an electrode is produced using the active material particle which covered solid-state-like lithium ion conductivity polymer beforehand. The electrolyte which dissolved lithium salt in the organic solvent or the organic solvent is infiltrated into the electrode, the solid-state-like polymer on the front face of an active material is dissolved in it, this is heated, and this polymer is made to gel by cooling.

[0023] At least one chosen from the group which consists of KETCHIEN black,

acetylene black, a graphite, a metal powder, plastic powder that covered the metal, and the end of a glass powder the metal was covered as an electric conduction agent used by this invention is effective. As a lithium ion conductivity inorganic solid electrolyte,  $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$ ,  $\text{Li}_{3.4}\text{V}_{0.6}\text{Si}_{0.4}\text{O}_4$ ,  $\text{LiTi}(\text{PO}_4)_3$ ,  $\text{LiPON}_x$  ( $0 < x \leq 1$ ) of amorphous nature,  $\text{LiX-Li}_2\text{S-Li}_2\text{O-P}_4\text{O}_{10-n}\text{Sn}$  (X is I or Br), etc. are effective.

[0024] As a positive active material in this invention,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoXNi}_{1-x}\text{O}_2$  ( $0 < x < 1$ ),  $\text{LiAlXNi}_{1-x}\text{O}_2$  ( $0 < x < 1$ ),  $\text{LiMnXNi}_{1-x}\text{O}_2$  ( $0 < x < 1$ ), Metallic oxides, such as  $\text{LiNiXMn}_2\text{O}_4$  ( $0 < x < 1$ ),  $\text{LiCoXMn}_2\text{O}_4$  ( $0 < x < 1$ ),  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ),  $\text{V}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ , and  $\text{NiOOH}$ , etc. can be used. at least one [ furthermore, ] chosen from the group which consists of B, Na, Mg, aluminum, P, calcium, Ti, Cr, Fe, Cu, Zn, and Ga -- the aforementioned metallic oxide -- 1 - 50at% -- the thing made to dissolve can also be used as a positive active material

[0025] Oxides, such as nitrides, such as charges of an alloy, such as carbon materials, such as a graphite in which the occlusion and discharge of the lithium by charge and discharge are possible as a negative-electrode active material in this invention, a TiSn alloy, and a TiSi alloy, and  $\text{LiCoN}$ , or  $\text{Li}_4/3\text{Ti}_5/3\text{O}_4$ , can be used.

#### \* NOTICES \*

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the lithium secondary battery equipped with the nonaqueous electrolyte of the shape of a liquid, a gel, or a solid-state.

[0002]

[Description of the Prior Art] In recent years, the need of the rechargeable battery as the power supply is very large with the rapid spread of portable devices, such as a personal computer and a cellular phone. Especially a lithium secondary battery is lightweight, it is observed as a rechargeable battery with which the high voltage is obtained, and development and utilization of various cells are advanced actively. The cell using the liquefied organic electrolyte which dissolved lithium salt in the organic solvent among lithium secondary batteries is

already completely put in practical use as an object for portable devices, and the cell using the polymer electrolyte of a gel is also put in practical use partly.

Furthermore, there are no worries about a liquid spill and research and development of the lithium secondary battery using the polymer solid electrolyte or the inorganic solid electrolyte of lithium ion conductivity are actively done aiming at the cell in which a miniaturization or thin-shape-izing is possible.

[0003] Generally, a negative-electrode active material expands at the time of charge of a lithium secondary battery, there is an inclination which a positive active material contracts, and there is an inclination which the reverse volume change produces at the time of electric discharge.  $\text{LiCoO}_2$  of a positive active material starts and  $\text{LiMn}_2\text{O}_4$  starts about 3.6% of volume change 3.2% on the usual charge-and-discharge conditions, for example. In alloy system negative electrodes, such as a TiSn alloy, a big cubical expansion happens especially at the time of charge.

[0004] Therefore, in the lithium secondary battery, change of the cell size by charge and discharge, especially expansion of a cell pose a practical big problem. Expansion and contraction of a cell also become the cause of destabilizing contact between electrode-cell containers and increasing the internal resistance of a cell. Furthermore, since the contact degree between components, such as an active material particle in an electrode, an electric conduction agent particle, and an electrolyte, becomes weaker while a positive electrode and a negative electrode repeat expansion and contraction by the charge-and-discharge cycle, there is a problem on which the charge/discharge capability ability in a high current deteriorates especially in a lithium secondary battery.

[0005] An inorganic solid electrolyte is made to contain also in an electrode in all the solid-state lithium secondary batteries that a lithium ion conductivity inorganic solid electrolyte layer is made to intervene between positive/negative poles, and are constituted. Since this inorganic solid electrolyte is hard powder, contact between the particles of an electrolyte and an active material is easy to be severed by expansion and contraction of the electrode by charge and discharge. Thereby, especially, with all solid-state lithium secondary batteries, supply of the lithium ion to an active material or the path of discharge is intercepted, and there is a problem to which the current in which charge and discharge are possible falls remarkably.

[0006] In order to solve this problem, all the solid-state lithium cells that covered the front face of an active material particle with lithium ion conductivity polymer are proposed (for example, JP, 11-7942, A). This aims at suppressing relaxation of junction between the particles by expansion and contraction of the active material in the inside of the electrode at the time of charge and discharge, and the volume change of a cell with the elasticity of the aforementioned polymer.

[0007] However, since the occupied volume of the polymer layer within an electrode is large when the front face of an active material particle is extensively covered with a polymer layer as indicated in the example, the volume of the opening formed between the active material particles in an electrode decreases remarkably. Therefore, since the polymer of the portion which was compressed

at the time of expansion of an active material, and deformed is hardly held in the aforementioned opening but expansion of an active material is reflected in expansion of an electrode as it is, the effect which suppresses expansion of an electrode is scarce. Moreover, since the whole surface of an active material particle is covered with the polymer layer, the network of the electronic conduction between active material particles becomes inadequate, and there is a problem to which a high charge-and-discharge property falls.

[0008]

[Problem(s) to be Solved by the Invention] this invention solves the problem of the above-mentioned conventional lithium secondary battery, and aims at degradation of change of the cell size by charge and discharge, increase of internal resistance, and the charge/discharge capability ability in a high current offering the lithium secondary battery suppressed effectively.

[0009]

[Means for Solving the Problem] The lithium secondary battery of this invention is characterized by covering partially the front face of one [ at least ] particle of a positive active material and a negative-electrode active material with lithium ion conductivity polymer. As for active material particle front faces other than the portion covered with the aforementioned lithium ion conductivity polymer, it is desirable to be covered with the electric conduction agent partially or extensively. As for active material particle front faces other than the portion covered with the aforementioned lithium ion conductivity polymer, it is still more desirable to be covered with the electric conduction agent and the lithium ion conductivity inorganic solid electrolyte partially or extensively.

[0010]

[Embodiments of the Invention] Drawing 1 is the cross section showing typically the active material particle which carried out covering processing of the front face by this invention. The front face of the active material particle 1 is partially covered with lithium ion conductivity polymer 2. Furthermore, if needed, the active material particle front faces of the portion which is not covered with the aforementioned polymer 2 are the electric conduction agent 3 and the lithium ion conductivity inorganic solid electrolyte 4, and are covered partially or extensively.

[0011] The lithium secondary battery of this invention makes it an indispensable condition to cover partially the front face of the particle of one [ at least ] active material of a positive active material and a negative-electrode active material with lithium ion conductivity polymer. Thereby, degradation of change of the cell size by charge and discharge, increase of internal resistance, and the charge/discharge capability ability in a high current can offer the lithium secondary battery suppressed effectively.

[0012] In this invention, since the layer of lithium ion conductivity polymer is wearing the active material particle front face partially unlike the aforementioned conventional technology (JP, 11-7942, A) and the occupied volume of the polymer layer within an electrode is small, volume of the opening formed between active material particles can be enlarged. When the polymer layer which has flexibility is compressed by this and it deforms by it at the time of expansion of an active material particle, the polymer for the variant part can be held in the

aforementioned opening. Thus, expansion of an electrode is eased by absorbing expansion of an active material and deformation of the polymer layer by it within an electrode.

[0013] Furthermore, at the time of contraction of an active material particle, when the polymer previously transformed by expansion of an active material particle reverts to the original form, change of an electrode size is eased. Thus, the volume change of the cell accompanying charge and discharge is eased, and when containing a cell to the predetermined space especially in a device, expansion of the cell which poses a problem can be suppressed effectively. The good contact between an electrode and a cell container is maintained simultaneously, and increase of the cell internal resistance by the charge-and-discharge cycle can be prevented.

[0014] In this invention, since the portions which are not covered with the polymer layer of the front face of an active material particle can be contacted within an electrode, the network of the electronic conduction between active material particles can fully be formed. Furthermore, since the active material particle is covered by the polymer of lithium ion conductivity, supply of the lithium ion to an active material particle or the path of discharge is fully secured. By these, the high charge-and-discharge property of a cell can be raised.

Furthermore, the junction nature between each particle in an electrode is strengthened by the binding capacity of the lithium ion conductivity polymer covered by the active material particle front face, and even when expansion and contraction of an active material arise at the time of charge and discharge, junction between the aforementioned particles is maintained. Thereby, the charge-and-discharge cycle life of a cell can be raised further.

[0015] As for the lithium secondary battery of this invention, it is desirable that active material particle front faces other than the portion covered with lithium ion conductivity polymer are covered with the electric conduction agent partially or extensively. By covering an active material particle front face with an electric conduction agent, the electronic-conduction nature between active material particles can be raised. Thereby, the internal resistance of a cell can be reduced further and the charge/discharge capability ability in a high current can be raised further.

[0016] As for the lithium secondary battery of this invention, it is still more desirable that active material particle front faces other than the portion covered with lithium ion conductivity polymer are covered with the electric conduction agent and the lithium ion conductivity inorganic solid electrolyte partially or extensively. The usual lithium ion inorganic solid electrolyte is equipped with the ionic conductivity of  $10^{-4}$  -  $10^{-5}$  ohm<sup>-1</sup> and cm higher 1-2 figures than solid-state-like lithium ion conductivity polymer. Thus, when ionic conductivity makes an inorganic high solid electrolyte adhere to an active material particle front face, the ion conductivity of the active material particle front face partially covered with lithium ion conductivity polymer can be raised further. The effect of the electric conduction agent which raises the electronic-conduction nature between active material particles can join this, and the charge/discharge capability ability in a high current can be raised further.

[0017] Generally, the ionic conductivity of lithium ion conductivity polymer of a solid-state-like thing is as low as  $10^{-5}$  -  $10^{-6}$  ohm<sup>-1</sup> and cm, and the thing of a gel shows  $10^{-3}$  -  $10^{-4}$  ohm<sup>-1</sup> and cm, and a high value. Therefore, when ionic conductivity uses the polymer of the shape of a comparatively low solid-state as lithium ion conductivity polymer, it is effective to use an inorganic solid electrolyte together as mentioned above in order to raise the ionic conductivity on the front face of an active material. When this method is applied to all solid-state lithium secondary batteries, a big effect is acquired especially.

[0018] The polymer of the shape of a solid-state which included lithium salt, such as LiBF<sub>4</sub>, LiPF<sub>6</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, and LiClO<sub>4</sub>, in at least one resin chosen from the group which consists of acrylonitrile system resins, such as polyester system resins, such as polyether system resins, such as a polyethylene oxide, and polyester terephthalate, an acrylic resin, acrylonitrile, and a vinyl acetate copolymer, and a polyvinylidene-fluoride resin as lithium ion conductivity polymer of this invention can be used.

[0019] There is the following method among the methods of covering an active material particle front face with the lithium ion conductivity polymer of the shape of an aforementioned solid-state partially. First, lithium salt is dissolved in the aforementioned resin which heats and carried out melting, and the powder of polymer is produced by the method of drying, while injecting after cooling the method of pulverizing, or the solution in which an aforementioned resin and aforementioned lithium salt were dissolved in hot blast etc. Subsequently, an active material particle front face is covered if needed using this polymer powder with the powder of an electric conduction agent and a lithium ion conductivity inorganic solid electrolyte. Under the present circumstances, polymer powder is wearing an active material particle front face partially, and the powder of an electric conduction agent and an inorganic solid electrolyte covers so that active material particle front faces other than the portion covered with polymer powder may be worn partially or extensively.

[0020] The method of putting in active material powder in equipment from active material powder with coating with a smaller particle size, i.e., polymer powder, polymer powder and the mixed powder of an electric conduction agent, or the powder that mixed inorganic solid electrolyte powder further, and performing covering processing mechanically as [ both ] the covering method, is desirable. As the method of mechanical covering processing, methods, such as the mechanical milling method by the hybridization method, the mechanofusion method, a planet ball mill, a ball mill, etc., can be taken. Otherwise, methods, such as chemical coating processing which deposits polymer powder and a metal electric conduction agent on an active material particle front face, can also be taken by non-electrolyzed compound plating in the dispersion liquid of polymer powder and a metal electric conduction agent.

[0021] The polymer of the gel which contains organic solvents, such as ethylene carbonate, polypropylene carbonate, ethyl methyl carbonate, dimethyl carbonate, and gamma-butyrolactone, or these mixed solvents in the lithium ion conductivity polymer of the shape of an above solid-state further as lithium ion conductivity polymer of this invention can also be used. Since ionic conductivity is high, the

gelled lithium ion conductivity polymer is much more effective in order to raise the high charge-and-discharge property of a cell.

[0022] The following method can be taken as a method of covering the lithium ion conductivity polymer of a gel partially on an active material particle front face.

First, an electrode is produced using the active material particle which covered solid-state-like lithium ion conductivity polymer beforehand. The electrolyte which dissolved lithium salt in the organic solvent or the organic solvent is infiltrated into the electrode, the solid-state-like polymer on the front face of an active material is dissolved in it, this is heated, and this polymer is made to gel by cooling.

[0023] At least one chosen from the group which consists of KETCHIEN black, acetylene black, a graphite, a metal powder, plastic powder that covered the metal, and the end of a glass powder the metal was covered as an electric conduction agent used by this invention is effective. As a lithium ion conductivity inorganic solid electrolyte,  $\text{Li}_3.6\text{Si}_0.6\text{P}_0.4\text{O}_4$ ,  $\text{Li}_3.4\text{V}_0.6\text{Si}_0.4\text{O}_4$ ,  $\text{LiTi}(\text{PO}_4)_3$ ,  $\text{LiPON}_x$  ( $0 < x \leq 1$ ) of amorphous nature,  $\text{LiX-Li}_2\text{S-Li}_2\text{O-P}_4\text{O}_{10}\text{-nSn}$  (X is I or Br), etc. are effective.

[0024] As a positive active material in this invention,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoXNi}_1\text{-XO}_2$  ( $0 < x < 1$ ),  $\text{LiAlXNi}_1\text{-XO}_2$  ( $0 < x < 1$ ),  $\text{LiMnXNi}_1\text{-XO}_2$  ( $0 < x < 1$ ), Metallic oxides, such as  $\text{LiNiXMn}_2\text{-XO}_4$  ( $0 < x < 1$ ),  $\text{LiCoXMn}_2\text{-XO}_4$  ( $0 < x < 1$ ),  $\text{Li}_1\text{+XMn}_2\text{-XO}_4$  ( $0 < x < 1$ ),  $\text{V}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ , and  $\text{NiOOH}$ , etc. can be used. at least one [ furthermore, ] chosen from the group which consists of B, Na, Mg, aluminum, P, calcium, Ti, Cr, Fe, Cu, Zn, and Ga -- the aforementioned metallic oxide -- 1 - 50at% -- the thing made to dissolve can also be used as a positive active material

[0025] Oxides, such as nitrides, such as charges of an alloy, such as carbon materials, such as a graphite in which the occlusion and discharge of the lithium by charge and discharge are possible as a negative-electrode active material in this invention, a TiSn alloy, and a TiSi alloy, and  $\text{LiCoN}$ , or  $\text{Li}_4/3\text{Ti}_5 / 3\text{O}_4$ , can be used.

[0026]

[Example] Next, an example explains this invention concretely.

[0027] <<example 1>>  $\text{LiClO}_4$  [ 5g ] was dissolved into the solution which dissolved polyethylene-oxide 30g in acetonitrile 600ml, and the lithium ion conductivity polymer solution was prepared. Next, it was made to dry and solidify, spraying this solution into hot blast, and lithium ion conductivity polymer powder with a particle size of about 0.3 micrometers was produced. After fully mixing 1g of this powder, 30g of  $\text{LiCoO}_2$  powder with a particle size of about 10 micrometers which is a positive active material, and 0.2g of aluminum powder with a particle size of 0.1 micrometers, the planet ball mill performed covering processing of an active material particle front face for 1 minute. This covered the front face of a positive-active-material particle with lithium ion conductivity polymer powder and aluminum powder partially.

[0028] 10g [ of positive-active-material powder after this covering processing ] and acetylene black 0.3g and 0.8g of fluororesin powder were fully mixed in the acetone, and the positive-electrode paste was prepared. This positive-electrode paste was applied to the collecting electrode plate made from aluminum foil, after

drying, it pressurized by the roll press, this was dried in the 60-degree C vacuum, and the positive-electrode board was produced. This was pierced and processed and the disc-like positive electrode with a diameter of 20mm was produced.

[0029] Subsequently, after fully mixing the 1g of the same lithium ion conductivity polymer powder as the case where a positive-active-material particle is covered with 20g of artificial graphites of 20 micrometers of mean particle diameters which are a negative-electrode active material, the ball mill performed covering processing for 1 minute. This covered partially the front face of a negative-electrode active material particle with lithium ion conductivity polymer powder. 10g [ of negative-electrode active material powder after this covering processing ] and acetylene black 0.1g and 1g of fluororesin powder were fully mixed in the acetone, and the negative-electrode paste was produced. This negative-electrode paste was applied on the charge collector made from Cu foil, after dryness, it pressurized by the roll press and the negative-electrode board was produced. This negative-electrode board was dried in the 60-degree C vacuum, it pierced to disc-like [ with a diameter of 21mm ], and the negative electrode was produced.

[0030] Next, after having carried out the laminating of a positive electrode, separator, and the negative electrode, containing in the cell case made from stainless steel and pouring an electrolyte into this, the obturation board was made to fit into opening of a cell case through a gasket, the crimp seal was performed, and the coin type cell was produced. The porous membrane made of a polyolefine system resin of 25 micrometers of thickness was used for separator. The organic electrolyte which dissolved mol [ of  $\text{LiClO}_4$  / 1 / ] in the solvent which mixed ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:40:40l. was used for the electrolyte.

[0031] Example of <<comparison 1>> The positive-active-material particle and the negative-electrode active material particle produced the coin type cell like the example 1 except not performing covering processing.

[0032] The charge-and-discharge cycle examination was performed using the coin type cell of an example 1 and the example 1 of comparison. Charge-and-discharge temperature was made into 20 degrees C, current 0.2CA and constant-current charge of upper limit voltage 4.1V were performed, and current 1CA and constant-current discharge of final-voltage 3.0V were performed. The number of charge-and-discharge cycles until service capacity turns into 70% of initial capacity was made into the cycle life. Consequently, to the cycle lives of the example 1 of comparison being 500 cycles, in the example 1, it is 680 cycles and the remarkable effect of the improvement in a cycle life of the cell by this invention was accepted.

[0033] <<example 2>> After adding 4g  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  to 30g of acrylonitrile resins, the temperature up was carried out to 140 degrees C, melting of the above-mentioned resin was carried out, and  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  was completely melted in this resin. Next, apply this fused resin on a glass substrate, cool, and it was made to solidify, and was made the shape of a film. This film was ground mechanically and lithium ion conductivity polymer powder with a particle size of about 0.3 micrometers was produced.

[0034] Next, after adding the 2g of the above-mentioned lithium ion conductivity polymer powder, and 0.4g of KETCHIEN black powder with a particle size of 0.02 micrometers and fully mixing to 2OLiMn4 powder with a particle size of 15 micrometers which is a positive active material, covering processing for 2 minutes was performed by the mechanofusion method. This covered the front face of a positive-active-material particle with lithium ion conductivity polymer powder and KETCHIEN black powder partially. The positive electrode was produced by the same method as an example 1 using the positive-electrode paste which was fully mixed and prepared in the acetone 10g of positive active materials which performed this covering processing, acetylene black 0.3g, and 0.8g of fluororesins.

[0035] Next, 5g of Ti powder and 119g of Sn powder were mixed for ten days with the ball mill by nitrogen-gas-atmosphere mind, and the TiSn alloy-powder end of 15-micrometer particle size was produced. After fully mixing 20g, the 5g of the same lithium ion conductivity polymer powder as having used for covering processing of a positive-active-material particle, and 0.2g of copper powders with a particle size of 0.1 micrometers the aforementioned alloy-powder end as a negative-electrode active material, covering processing was performed for 5 minutes using the equipment for mechano fusions (product made from Nara Machine : Sita composer). The negative electrode was produced by the same method as an example 1 using the negative-electrode active material powder which performed this covering processing.

[0036] The coin type cell was produced like the example 1 using an above-mentioned positive electrode and an above-mentioned negative electrode. However, the organic electrolyte which dissolved mol [ of  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{Ns}$  / 1.2 / ] in the solvent which mixed ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:30:50l. was used for the electrolyte.

[0037] Example of <<comparison 2>> The positive-active-material particle and the negative-electrode active material particle produced the coin type cell like the example 2 except not performing covering processing.

[0038] The charge-and-discharge cycle examination was performed by the same method as an example 1 using the coin type cell of an example 2 and the example 2 of comparison. Consequently, to the cycle lives of the example 2 of comparison being 50 cycles, in the example 2, it is 550 cycles and it was checked that the cycle life of a cell improves sharply by this invention.

[0039] <<example 3>> LiNiO<sub>2</sub> 10g with a particle size [ as a positive active material ] of 12 micrometers, acetylene black 0.3g, and 0.8g of fluororesins were fully mixed in the acetone, and the positive-electrode paste was prepared. The positive electrode was produced by the same method as an example 1 using this positive-electrode paste.

[0040] Next, 30g of polymethacrylate resins was dissolved in acetone 600ml, LiPF<sub>4</sub> 4g was dissolved in the solution, and the lithium ion conductivity polymer solution was prepared. Lithium ion conductivity polymer powder with a particle size of about 0.3 micrometers was produced by the same method as an example 1 using this polymer solution. The acetone was volatilized mixing and stirring 2g [ of this polymer powder ], 10g [ of LiCo<sub>3</sub>-xNx powder as a negative-electrode

active material ], 2g [ of  $\text{SnO}_2$  powder ], and acetylene black 0.5g in an acetone, and it dried in the 60 more-degree C vacuum. By covering processing of this negative-electrode active material particle, the negative-electrode active material powder by which the front face was extensively covered by lithium ion conductivity polymer powder and the electric conduction agent was produced. Next, the negative electrode was produced by the same method as an example 1 using the negative-electrode active material powder which performed this covering processing.

[0041] The coin type cell was produced like the example 1 using an above-mentioned positive electrode and an above-mentioned negative electrode. However, the organic electrolyte which carried out 1 mol/l dissolution of  $\text{LiPF}_6$  was used for the solvent which mixed ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:30:50 at the electrolyte.

[0042] Example of <<comparison 3>> The positive-active-material particle and the negative-electrode active material particle produced the coin type cell like the example 3 except not performing covering processing.

[0043] The charge-and-discharge cycle examination was performed by the same method as an example 1 using the coin type cell of an example 3 and the example 3 of comparison. Consequently, to the cycle lives of the example 3 of comparison being 300 cycles, in the example 3, it is 600 cycles and it was checked that the cycle life of a cell improves sharply by this invention.

[0044] <<example 4>> Except having used the acetone as a solvent instead of the acetonitrile, it is the same method as an example 1, and lithium ion conductivity polymer powder with a particle size of about 0.3 micrometers was produced. Next, after mixing 2g [ of  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  powder with a particle size / as 0.5g of this polymer powder, 0.50210g of  $\text{LiCo}_0.5\text{nickel}$  with a particle size / as a positive active material / of 10 micrometers, and a lithium ion conductivity inorganic solid electrolyte / of 0.2 micrometers ], and acetylene black 0.3g, covering processing of a positive-active-material particle was performed by the same method as an example 1. This covered partially lithium ion conductivity polymer powder, the electric conduction agent, and the inorganic solid electrolyte on the front face of  $0.50\text{LiCo}_0.5\text{nickel}_2$  particle.

[0045] 10g [ of positive-active-material particles which performed this covering processing ], and acetylene black 0.3g, and 0.8g of fluororesins were fully mixed in the acetone, and the positive-electrode paste was produced. The positive electrode was produced by the same method as an example 1 using this positive-electrode paste. The negative electrode was produced by the same method as an example 1 as lithium salt added to lithium ion conductivity polymer except having used  $\text{LiPF}_6$  instead of  $\text{LiClO}_4$ .

[0046] An above-mentioned positive electrode and an above-mentioned negative electrode were pressurized through the inorganic solid electrolyte pellet, and unification molding was performed. This was contained in the cell case, the obturation board was fitted into opening of a case through the gasket, and all coin type solid-state lithium secondary batteries were produced by bending and obturating opening. What carried out pressing of the  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  powder to disc-like [ with a diameter / of 22mm / and a thickness of 20 micrometers ] was

used for the electrolyte pellet.

[0047] Example of <<comparison 4>> The positive-active-material particle and the negative-electrode active material particle produced all coin type solid-state lithium cells like the example 4 except not performing covering processing.

[0048] The charge-and-discharge cycle examination was performed by the same method as an example 1 using the coin type cell of an example 4 and the example 4 of comparison. Consequently, to the cycle lives of the example 4 of comparison being 600 cycles, in the example 4, it is 1000 cycles and it was checked that the cycle life of a cell improves sharply by this invention. Moreover, the ratio of the service capacity in the case of 2C electric discharge to the service capacity in the case of 1C electric discharge was 40% in the example 4 of comparison 95% in the example 4. Thereby, the remarkable effect of the improvement in a high-rate-discharge property by this invention was checked.

[0049] <<example 5>> First, after fitting into a cell case, the temporary seal mouth of the obturation board is carried out loosely, the organic electrolyte was infiltrated into the polymer powder of an active material particle front face, and this polymer was made to gel by heating this for 30 minutes at 70 degrees C in the obturation process at the time of producing a coin type cell. Final obturation was performed after that. The coin type cell was produced like the example 2 except this obturation process.

[0050] As a result of performing a charge-and-discharge cycle examination by the same method as an example 1 using the coin type cell of an example 5, the cycle life of 750 cycle was acquired to 550 cycles of an example 2. Thereby, when it was a gel rather than the ion conductivity polymer which covers an active material particle front face partially is a solid-state-like, it was checked that a cycle life improves more effectively.

[0051]

[Effect of the Invention] By this invention, the dimensional change of a lithium secondary battery and the increase of internal resistance by charge and discharge can be suppressed effectively. Furthermore, a high-rate-discharge property and a cycle life are sharply improvable.

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[Translation done.]

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## EXAMPLE

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[Example] Next, an example explains this invention concretely.

[0027] <<example 1>>  $\text{LiClO}_4$  [ 5g ] was dissolved into the solution which dissolved polyethylene-oxide 30g in acetonitrile 600ml, and the lithium ion conductivity polymer solution was prepared. Next, it was made to dry and solidify, spraying this solution into hot blast, and lithium ion conductivity polymer powder with a particle size of about 0.3 micrometers was produced. After fully mixing 1g of this powder, 30g of  $\text{LiCoO}_2$  powder with a particle size of about 10

micrometers which is a positive active material, and 0.2g of aluminum powder with a particle size of 0.1 micrometers, the planet ball mill performed covering processing of an active material particle front face for 1 minute. This covered the front face of a positive-active-material particle with lithium ion conductivity polymer powder and aluminum powder partially.

[0028] 10g [ of positive-active-material powder after this covering processing ] and acetylene black 0.3g and 0.8g of fluororesin powder were fully mixed in the acetone, and the positive-electrode paste was prepared. This positive-electrode paste was applied to the collecting electrode plate made from aluminum foil, after drying, it pressurized by the roll press, this was dried in the 60-degree C vacuum, and the positive-electrode board was produced. This was pierced and processed and the disc-like positive electrode with a diameter of 20mm was produced.

[0029] Subsequently, after fully mixing the 1g of the same lithium ion conductivity polymer powder as the case where a positive-active-material particle is covered with 20g of artificial graphites of 20 micrometers of mean particle diameters which are a negative-electrode active material, the ball mill performed covering processing for 1 minute. This covered partially the front face of a negative-electrode active material particle with lithium ion conductivity polymer powder. 10g [ of negative-electrode active material powder after this covering processing ] and acetylene black 0.1g and 1g of fluororesin powder were fully mixed in the acetone, and the negative-electrode paste was produced. This negative-electrode paste was applied on the charge collector made from Cu foil, after dryness, it pressurized by the roll press and the negative-electrode board was produced. This negative-electrode board was dried in the 60-degree C vacuum, it pierced to disc-like [ with a diameter of 21mm ], and the negative electrode was produced.

[0030] Next, after having carried out the laminating of a positive electrode, separator, and the negative electrode, containing in the cell case made from stainless steel and pouring an electrolyte into this, the obturation board was made to fit into opening of a cell case through a gasket, the crimp seal was performed, and the coin type cell was produced. The porous membrane made of a polyolefine system resin of 25 micrometers of thickness was used for separator. The organic electrolyte which dissolved mol [ of  $\text{LiClO}_4$  / 1 / l ] in the solvent which mixed ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:40:40l. was used for the electrolyte.

[0031] Example of <<comparison 1>> The positive-active-material particle and the negative-electrode active material particle produced the coin type cell like the example 1 except not performing covering processing.

[0032] The charge-and-discharge cycle examination was performed using the coin type cell of an example 1 and the example 1 of comparison. Charge-and-discharge temperature was made into 20 degrees C, current 0.2CA and constant-current charge of upper limit voltage 4.1V were performed, and current 1CA and constant-current discharge of final-voltage 3.0V were performed. The number of charge-and-discharge cycles until service capacity turns into 70% of initial capacity was made into the cycle life. Consequently, to the cycle lives of the example 1 of comparison being 500 cycles, in the example 1, it is 680 cycles

and the remarkable effect of the improvement in a cycle life of the cell by this invention was accepted.

[0033] <<example 2>> After adding 4g  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  to 30g of acrylonitrile resins, the temperature up was carried out to 140 degrees C, melting of the above-mentioned resin was carried out, and  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  was completely melted in this resin. Next, apply this fused resin on a glass substrate, cool, and it was made to solidify, and was made the shape of a film. This film was ground mechanically and lithium ion conductivity polymer powder with a particle size of about 0.3 micrometers was produced.

[0034] Next, after adding the 2g of the above-mentioned lithium ion conductivity polymer powder, and 0.4g of KETCHIEN black powder with a particle size of 0.02 micrometers and fully mixing to 20LiMn4 powder with a particle size of 15 micrometers which is a positive active material, covering processing for 2 minutes was performed by the mechanofusion method. This covered the front face of a positive-active-material particle with lithium ion conductivity polymer powder and KETCHIEN black powder partially. The positive electrode was produced by the same method as an example 1 using the positive-electrode paste which was fully mixed and prepared in the acetone 10g of positive active materials which performed this covering processing, acetylene black 0.3g, and 0.8g of fluororesins.

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[0036] The coin type cell was produced like the example 1 using an above-mentioned positive electrode and an above-mentioned negative electrode. However, the organic electrolyte which dissolved mol [ of  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{Ns}$  / 1.2 / ] in the solvent which mixed ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:30:50l. was used for the electrolyte.

[0037] Example of <<comparison 2>> The positive-active-material particle and the negative-electrode active material particle produced the coin type cell like the example 2 except not performing covering processing.

[0038] The charge-and-discharge cycle examination was performed by the same method as an example 1 using the coin type cell of an example 2 and the example 2 of comparison. Consequently, to the cycle lives of the example 2 of comparison being 50 cycles, in the example 2, it is 550 cycles and it was checked that the cycle life of a cell improves sharply by this invention.

[0039] <<example 3>>  $\text{LiNiO}_2$  10g with a particle size [ as a positive active material ] of 12 micrometers, acetylene black 0.3g, and 0.8g of fluororesins were

fully mixed in the acetone, and the positive-electrode paste was prepared. The positive electrode was produced by the same method as an example 1 using this positive-electrode paste.

[0040] Next, 30g of polymethacrylate resins was dissolved in acetone 600ml, LiPF<sub>4</sub> was dissolved in the solution, and the lithium ion conductivity polymer solution was prepared. Lithium ion conductivity polymer powder with a particle size of about 0.3 micrometers was produced by the same method as an example 1 using this polymer solution. The acetone was volatilized mixing and stirring 2g [ of this polymer powder ], 10g [ of LiCo<sub>3-x</sub>N<sub>x</sub> powder as a negative-electrode active material ], 2g [ of SnO<sub>2</sub> powder ], and acetylene black 0.5g in an acetone, and it dried in the 60 more-degree C vacuum. By covering processing of this negative-electrode active material particle, the negative-electrode active material powder by which the front face was extensively covered by lithium ion conductivity polymer powder and the electric conduction agent was produced. Next, the negative electrode was produced by the same method as an example 1 using the negative-electrode active material powder which performed this covering processing.

[0041] The coin type cell was produced like the example 1 using an above-mentioned positive electrode and an above-mentioned negative electrode. However, the organic electrolyte which carried out 1 mol/l dissolution of LiPF<sub>6</sub> was used for the solvent which mixed ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate by the volume ratio of 20:30:50 at the electrolyte.

[0042] Example of <<comparison 3>> The positive-active-material particle and the negative-electrode active material particle produced the coin type cell like the example 3 except not performing covering processing.

[0043] The charge-and-discharge cycle examination was performed by the same method as an example 1 using the coin type cell of an example 3 and the example 3 of comparison. Consequently, to the cycle lives of the example 3 of comparison being 300 cycles, in the example 3, it is 600 cycles and it was checked that the cycle life of a cell improves sharply by this invention.

[0044] <<example 4>> Except having used the acetone as a solvent instead of the acetonitrile, it is the same method as an example 1, and lithium ion conductivity polymer powder with a particle size of about 0.3 micrometers was produced. Next, after mixing 2g [ of Li<sub>3</sub>PO<sub>4</sub>-Li<sub>2</sub> S-SiS<sub>2</sub> powder with a particle size / as 0.5g of this polymer powder, 0.50210g of LiCo<sub>0.5</sub>nickel with a particle size / as a positive active material / of 10 micrometers, and a lithium ion conductivity inorganic solid electrolyte / of 0.2 micrometers ], and acetylene black 0.3g, covering processing of a positive-active-material particle was performed by the same method as an example 1. This covered partially lithium ion conductivity polymer powder, the electric conduction agent, and the inorganic solid electrolyte on the front face of 0.50LiCo<sub>0.5</sub>nickel<sub>2</sub> particle.

[0045] 10g [ of positive-active-material particles which performed this covering processing ], and acetylene black 0.3g, and 0.8g of fluororesins were fully mixed in the acetone, and the positive-electrode paste was produced. The positive electrode was produced by the same method as an example 1 using this positive-electrode paste. The negative electrode was produced by the same

method as an example 1 as lithium salt added to lithium ion conductivity polymer except having used LiPF<sub>6</sub> instead of LiClO<sub>4</sub>.

[0046] An above-mentioned positive electrode and an above-mentioned negative electrode were pressurized through the inorganic solid electrolyte pellet, and unification molding was performed. This was contained in the cell case, the obturation board was fitted into opening of a case through the gasket, and all coin type solid-state lithium secondary batteries were produced by bending and obturating opening. What carried out pressing of the Li<sub>3</sub>PO<sub>4</sub>-Li<sub>2</sub>S-SiS<sub>2</sub> powder to disc-like [ with a diameter / of 22mm / and a thickness of 20 micrometers ] was used for the electrolyte pellet.

[0047] Example of <<comparison 4>> The positive-active-material particle and the negative-electrode active material particle produced all coin type solid-state lithium cells like the example 4 except not performing covering processing.

[0048] The charge-and-discharge cycle examination was performed by the same method as an example 1 using the coin type cell of an example 4 and the example 4 of comparison. Consequently, to the cycle lives of the example 4 of comparison being 600 cycles, in the example 4, it is 1000 cycles and it was checked that the cycle life of a cell improves sharply by this invention. Moreover, the ratio of the service capacity in the case of 2C electric discharge to the service capacity in the case of 1C electric discharge was 40% in the example 4 of comparison 95% in the example 4. Thereby, the remarkable effect of the improvement in a high-rate-discharge property by this invention was checked.

[0049] <<example 5>> First, after fitting into a cell case, the temporary seal mouth of the obturation board is carried out loosely, the organic electrolyte was infiltrated into the polymer powder of an active material particle front face, and this polymer was made to gel by heating this for 30 minutes at 70 degrees C in the obturation process at the time of producing a coin type cell. Final obturation was performed after that. The coin type cell was produced like the example 2 except this obturation process.

[0050] As a result of performing a charge-and-discharge cycle examination by the same method as an example 1 using the coin type cell of an example 5, the cycle life of 750 cycle was acquired to 550 cycles of an example 2. Thereby, when it was a gel rather than the ion conductivity polymer which covers an active material particle front face partially is a solid-state-like, it was checked that a cycle life improves more effectively.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is drawing of longitudinal section of the active material particle which carried out covering processing of the front face by this invention.

[Description of Notations]

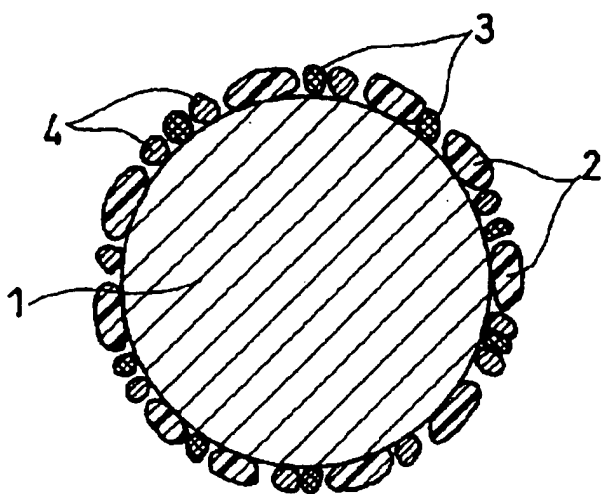
1 Active Material Particle

2 Lithium Ion Conductivity Polymer

3 Electric Conduction Agent

#### 4 Lithium Ion Conductivity Inorganic Solid Electrolyte

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- 1 活物質粒子
- 2 リチウムイオン伝導性ポリマー
- 3 導電剤
- 4 リチウムイオン伝導性無機固体電解質

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#### CLAIMS

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##### [Claim(s)]

[Claim 1] The lithium secondary battery with which the front face of one [ at least ] particle of a positive active material and a negative-electrode active material is characterized by being partially covered with lithium ion conductivity polymer.

[Claim 2] The lithium secondary battery according to claim 1 by which active material particle front faces other than the portion covered with the aforementioned lithium ion conductivity polymer are covered partially or extensively by the electric conduction agent.

[Claim 3] The lithium secondary battery according to claim 1 by which active material particle front faces other than the portion covered with the aforementioned lithium ion conductivity polymer are covered partially or extensively by the electric conduction agent and the lithium ion conductivity inorganic solid electrolyte.

[Claim 4] At least one chosen from the group which the aforementioned lithium ion conductivity polymer becomes from a polyether system resin, a polyester system resin, an acrylic resin, a polyacrylate system resin, and a polyvinylidene-

fluoride resin, and the lithium secondary battery according to claim 1 to 3 with which it consists of lithium salt.

[Claim 5] The lithium secondary battery according to claim 1 to 3 which is the polymer of the gel which the aforementioned lithium ion conductivity polymer becomes from at least one chosen from the group which consists of a polyether system resin, a polyester system resin, an acrylic resin, a polyacrylate system resin, and a polyvinylidene-fluoride resin, lithium salt, and an organic solvent.

[Claim 6] The lithium secondary battery according to claim 2 to 5 which is at least one chosen from the group which the aforementioned electric conduction agent becomes from KETCHIEN black, acetylene black, a graphite, a metal powder, metallic-coating plastic powder, and the end of a metallic-coating glass powder.

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[Translation done.]